A

PROJECT REPORT

ON

Removal of Malachite Green dye by adsorption using char

Submitted to the
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In partial fulfillment of the requirements

Of
Bachelor of Technology (Chemical Engineering)

By

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UNDER THE GUIDANCE OF:
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CERTIFICATE

This is to certify that the thesis on "**Removal of Malachite Green dye by adsorption using char**" is submitted by **Chetna Parashar (108CH036)** to National Institute of Technology, Rourkela under my supervision and is worthy for the partial fulfillment of the degree of Bachelor of Technology (Chemical Engineering) of the Institute. She has fulfilled all the prescribed requirements and the report, which is based on candidate's own work, has not been submitted elsewhere.

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Chetna Parashar

ABSTRACT

The objective of this project work is to study the adsorption of Malachite Green dye using char. Cheap and eco-friendly adsorbent has been used for removal of malachite green dye from aqueous solution. Liquid phase batch operations were carried out to observe the effect of various experimental parameters such as contact time, temperature, pH, initial concentration of malachite green and adsorbate dose and the optimum conditions for these parameters were evaluated. Various characteristics of char made out of Sheesham seeds were examined. Study on adsorption kinetic and adsorption isotherm was carried out and best fitting models for rate kinetics and isotherms were suggested. Comparisons with other available low cost adsorbents were also done. This project work can help in designing low cost adsorption columns for treating effluent water in industries or other adsorption processes.

KEYWORDS: adsorption, isotherm, rate kinetics, char, dye.

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CHAPTER-01

INTRODUCTION

1. INTRODUCTION

A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics [1], [3]. It appears to be colored because they absorb some wavelengths of light in particular than other. Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants [2, 3] .These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non-biodegradable due to their complex molecular structures making them more stable and hard to biodegrade [1, 2]. They cause water pollution and also pose a serious threat to environment. These colored stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem [2, 3]. Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms [1, 2].

The main source of discharge of dyes is textile industries where they are used to color products. Today there are over 1, 00,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually [1]. The types of dyes are mainly basic dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes [1, 2].Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. They don't fade by water or sunlight and owing to their complexity in structures; they can't be adequately treated in conventional treatment plants for waste waters [2].

There are innumerous harmful effects of dyes on ecosystem such as: (1) they pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes [1, 2]. (2) They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities [1, 2]. (3) They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes [1, 2]. (4) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations. (5) Consume dissolved oxygen and affect aquatic ecosystem [2]. (5) Sequester metal ions which produce micro toxicity to aquatic lives.

There are various ways to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. Many of these processes are not so popular due to their economic disadvantages and inefficiency [25]. Coagulations and chemical and electrochemical oxidations have low feasibility on large scale plants [25]. Adsorption is preferred over these processes and is widely used due to low cost and high performance [25]. Common adsorbents are activated carbon, alumina silica and metal hydroxides. Economic advantages, performance efficiencies and environment are the main concerns when selecting a adsorbent, thus researchers generally go for using low-cost adsorbents like char from agricultural wastes and others [25].

1.1 OBJECTIVE

The purpose of this project work is:

- To determine effectiveness of removing malachite green dye using char and to study effects of various experimental parameters on adsorption.
- To investigate potential use of char and to find out the conditions for improved performance of Sheesham seeds char in removing dye.
- To carry out adsorption kinetic and isotherm studies of removal of dye using char.

1.2 SCOPE

- Study of effects of various experimental parameters on adsorption like
    - Effect of contact time
    - Effect of temperature
    - Effect of pH
    - Effect of adsorbent dose
    - Effect of initial concentration of Malachite green[25]

- Adsorption kinetic study
- Adsorption isotherm study

1.3 PROBLEM STATEMENT

In present time, many industries commonly use activated carbon as adsorbent agent for dye removal. The cost of activated carbon and associated problems of regeneration of activated carbon has forced a new research to find other alternative low cost adsorbents agents.

Nowadays, there are numerous numbers of low cost, commercially available adsorbents which have been used for dye removal. Moreover as the adsorption capacities of the various adsorbents are not very large, the new adsorbents which are more economical, easily available and highly effective are still needed so the work is still going on. Sheesham seeds are found in abundance in India so the char made out of seeds of Sheesham seeds can be seen as a potential source of adsorbent for adsorption columns of industries.

CHAPTER-2

LITERATURE REVIEW

2. LITERATURE REVIEW

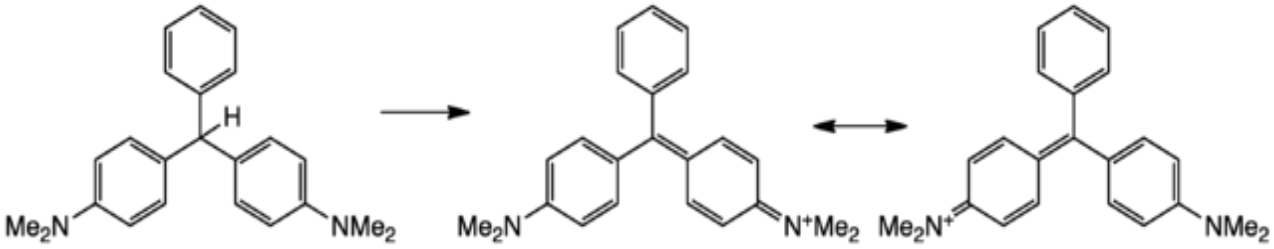
2.1 ADSORBATE

Malachite green dye is basically a cationic dye. It is usually prepared by the condensation of Benzaldehyde and dimethylamine to give leuco malachite green LMG [1, 2]:

$C_6H_5CHO + 2\ C_6H_5N\ (CH_3)_2 \rightarrow C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + H_2O$ [25]

Then this compound is oxidized to a cation that is MG

$C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + HCl + 1/2\ O_2 \rightarrow [C_6H_5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl + H_2O$ [25]



2.2 ADSORBENT

Shesham trees are found in abundance in India and char of their seeds can be used as a low-cost adsorbent to remove dyes.

2.3 ADSORPTION

It is the process of formation of a layer of solid or gas on the substrate. It involves separation of a substance from fluid phase by accumulation on the substrate of solid phase [3].

2.4 MECHANISM OF ADSORPTION

Adsorption is a three step process. At first the adsorbate diffuses from fluid stream to the external surface of adsorbent [3]. Secondly the adsorbate shifts to the pores of the adsorbent particles. Majority of adsorption occurs in these pores because of their large surface area. Finally the molecules adhere to the surface area of pores [3].

Adsorption is a surface phenomenon which results out of binding forces between atoms, molecules and ions of adsorbate and the surface of adsorbent [3].

2.5 ADSORPTION KINETICS

In order to investigate the controlling mechanisms of the adsorption processes like mass transfer and chemical reactions, pseudo first-order and pseudo second-order kinetic studies are used to test the experimental data[4].

The pseudo-first-order kinetic model has been given by "Lagergren" (1898) for the adsorption of solid or fluid systems and its formula is given as:

$$\frac{dq}{dt} = k_1(q_e - q_w)$$

After integrating we get;

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_t is the adsorption capacity at time't' (mg g^{-1}) and k_1 (min^{-1}) is the rate constant of the pseudo-first adsorption [4].

Ho's pseudo-second-order kinetic model is based on the assumption that the sorption follows second order chemisorption [4]. Pseudo-second-order kinetic model is given by;

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

After integration,

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second- order adsorption and q_t is the adsorption capacity at time't' (mg g^{-1}).

2.6 ADSORPTION KINETICS

Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface [4]. The adsorption processes are generally described by the Langmuir and the Freundlich isotherm models [4].

The Langmuir equation is based on the fact that there is no interaction between the adsorbate molecules and that the adsorption process is localized in a monolayer [4]. It then assumes that once a dye molecule occupies a given site, no more adsorption can take place at that site [4]. The Langmuir equation is commonly expressed as in the linear form:

$$\frac{1}{q_e} = \frac{1}{b * q_0 * C_e} + \frac{1}{q_0}$$

Where C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e is the equilibrium capacity of dye on the adsorbent (mg g−1), q_o is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}) and is related to the free energy of adsorption [4].

The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Its linear form can be written as:

$$\ln q_e = lnk_f + \frac{1}{n * lnC_e}$$

where k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicates the capacity and intensity of the adsorption, respectively.

The Temkin isotherm model is based on the fact that the heat of adsorption of all the molecules in a layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and also that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [5]. The Temkin isotherm is given as:

qe = BlnA + BlnCe [5]

where A (l/g) is the equilibrium binding constant, which corresponds to the maximum binding energy, and constant B is related to the heat of adsorption[10]. A plot of q_e versus lnCe enables the determination of the isotherm constants B and A from the slope and intercept of the straight line plot [5].

Since long time some solids have been used to remove dye from aqueous solution. Various scientists Brunauer, Emmet and Teller, Langmuir, McBain and Barrer in early twentieth century studied ways to remove contaminants from liquids and gases using solids [3].

In 2005 B.H.Hameed, A.T.M.Din, A.L.Ahmad carried out adsorption of methylene blue by bamboo-based activated carbon [6]. Bamboo was used to make activated carbon by physiochemical activation with potassium hydroxide and carbon dioxide [6]. Adsorptiobn models and kinetic studies were also conducted and it was found that pseudo-second-order model best described the process [6].

In 2005 I.D. Mall,V.C. Srivastava,N.K.Agarwal and I.M. Mishra studied the removal of malachite green dye from aqueous solution using bagasse fly ash and analyzed kinetic and adsorption isotherm models[7]. Adsorption was carried out in batch processes and the effects of various parameters were analyzed. Adsorption followed pseudo-second-order kinetics [7].

In 2006 Ewa Lorenc-Grabowska, Gra_zyna Gryglewicz conducted experiments on adsorption of Congo Red using bituminous coal-based mesoporous activated carbon[8]. Mesopores contribute 52 to 83% to the total pore volume. The adsorption was best described by pseudo-second-order

model and the Langmuir equation [8]. The monolayer adsorption was found to increase with increase in mesopore volume [8].

In 2007, R.A.Shawabkeh and E.S.M. Abu-Nameh performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells [9]. Activated carbon is prepared from pecan shells by chemical activation with phosphoric acid. Then it is treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells [9].

In 2008 B.H. Hameed, M.I. El-Khaiary studied the adsorption of Malachite green dye by rattan sawdust at 30^{o}C [14]. Results indicated that rattan sawdust can be used as low cost adsorbent source. Two isotherms Freundlich and Langmuir were analyzed and the best fit model was found to be Langmuir isotherm model. Adsorption kinetics was predicted by pseudo-first –order model. For a short period the adsorption rate was controlled by film diffusion, at longer adsorption period pore-diffusion controls the rate [14].

In 2009 feasibility of using degreased coffee beans as adsorbent for removing Malachite Green dye was evaluated by Mi-Hwa Baek, Christianah Olakitan Ijagbemi, Se-Jin O, Dong-Su Kim. Rate kinetics, adsorption isotherms and thermodynamic properties were also evaluated for the purpose [10].

In 2010, removal of Malachite Green dye from wastewater was studied by M. Anbia and A. Ghaffari using mesoporous carbon adsorbent [15]. Mesoporous carbon was synthesized and effects of various conditions such as dye concentration, adsorbent dose, contact time and pH were observed, the adsorption isotherms and rate kinetics were also determined [15].

In 2011 removal of Malachite Green present in aqueous solution by use of solid agricultural waste, was studied [12]. Agricultural solid waste, Kapok hull was activated by Sulphuric acid (1:1 ratio) and batch kinetic and isotherm experiments were performed to determine the sorption and desorption characteristics [12]. The experimental parameters affecting rate of adsorption were initial dye concentration, carbon dose, agitation time, particle size, and temperature and pH variation [12]. The adsorption isotherm models and rate kinetics were established for the process. Adsorption rate constants, diffusion rate constants, interparticle diffusion constants and diffusion coefficients were also determined. It was found out that interparticle diffusion is the rate limiting step [12].

CHAPTER-3

EXPERIMENTAL WORK

3. EXPERIMENTAL WORK

3.1 MATERIALS

3.1.1 ADSORBENT:

Sheesham seeds char is used as adsorbent for dye removal. Proximate analysis was done for char to know its characteristics. Also zeta potential was found out to know the surface potential of char.

Specifications:

Volatile matter 38.1%

Moisture content 3%

Ash content 24.5%

Fixed carbon 34.4%

Zeta potential -56.4 mV

Bulk density 446.1 kg/m^3

3.1.2 ADSORBATE

Malachite green dye is the adsorbate, its colour is green. It gives green colored solution in aqueous phase. It is a basic cationic dye. Its chemical formula is $C_{52}H_{54}N_4O_{12}$, molecular weight is 927, λ_{max}=618nm [1].

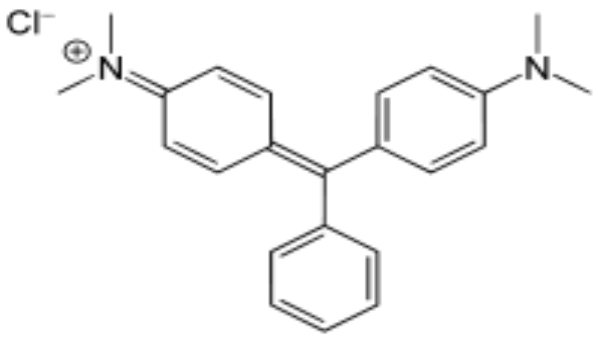


Fig 3.1: Structure of malachite green dye

3.2 EQUIPMENTS

3.2.1 GLASSWARE AND APPARATUS USED

Table 3.1: List of instruments, their make and use

INSTRUMENTS	**MAKE**	**USE**
Electronic weight balance	Sartorius	To measure weight
Shaker	Environmental orbital shaker	To stir the content
Oven	Shivaki	To dry the samples
pH meter	EuTech Instruments	To measure pH
Shaker	Environmental orbital shaker	To shake the sample in dye solution
Spectrophotometer	Jasco (V-530)	Absorbance
Muffle furnace		To carry out proximate analysis
Hot air Oven		To carry out proximate analysis
Zeta potential analyzer		To measure the zeta potential

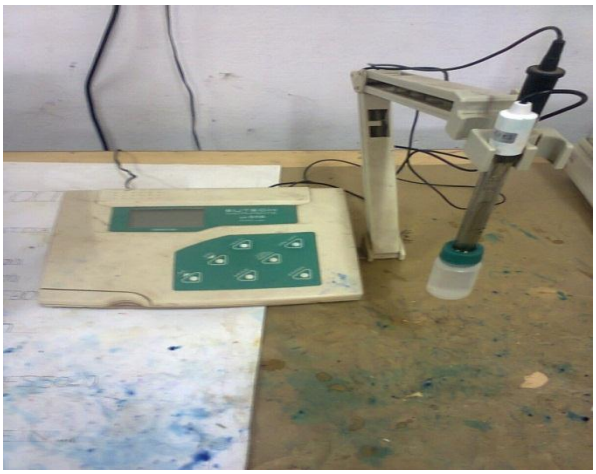


Fig 3.2: pH meter

Fig 3.3: Glasswares

Fig 3.4: Incubator shaker

Fig 3.5: Muffle furnace

Fig 3.6 : Hot air oven

Fig 3.7: Zeta potential analyzer

3.3 METHODS:

3.3.1 PROXIMATE ANALYSIS OF CHAR

3.3.1.1 MOISTURE CONTENT:

A crucible with lid was taken and weighed. 2 gm of sample was taken in the crucible with lid and weighed. It was kept in hot air oven at 155^{o}C for 2 and1/2 hours. It was taken out and kept in the dessicator. Then the weight was taken out.

$$\boldsymbol{M = 100 * \frac{(B - F)}{(B - G)}}$$

M= moisture content

B= mass of crucible with lid plus sample

F=mass of crucible with lid plus dried sample.

G= mass of crucible with lid

B= 39.40

F=39.34

G=37.40

Moisture content was 3%

3.3.1.2 ASH CONTENT

A crucible was taken and weighed. 2gm of sample of char was taken in crucible and weighed. The sample was kept in a muffle furnace for 3 hrs at temperature 650^0C. Then it was taken out and kept in a desiccator for half an hour to cool down. Then the weight is taken.

$$\boldsymbol{A = 100 * \frac{(F - G)}{(B - G)}}$$

G=Mass of empty crucible

B= mass of crucible plus sample

F= mass of crucible plus ashed sample

G= 36.81

B=38.80

F=37.30

Thus ash content is calculated to be 24.5%

3.3.1.3 VOLATILE MATTER:

A crucible with lid was taken and weighed. 1 gm of char sample was taken in the crucible with lid and weighed. It was kept in the muffle furnace for 7 minutes. Then it was taken out and kept in the dessicator for half an hour to cool down. The weight of the sample in crucible with lid was taken.

% volatile matter was then calculated

$$\boldsymbol{V = 100 * \frac{100 * (B - F) - M * (B - G)}{(B - G) * (100 - M)}}$$

Where, B= mass of crucible with lid plus sample

G=Mass of empty crucible

F= mass of crucible with lid plus ashed sample

M=moisture content

B=37.87

F=37.47

M=3

G=36.87

%volatile matter was 38.1%

3.3.1.4 CARBON CONTENT

Carbon content is calculated by

% CARBON =100 – (%VOLATILE MATTER+%MOISTURE CONTENT+ %ASH)

% carbon content was calculated to be 34.4%.

3.3.2. ZETA POTENTIAL

Sample of char was dissolved in distilled water and sonicated and then its zeta potential was measured by the instrument. Zeta potential was calculated to be -56 mV.

3.3.3. BULK DENSITY:

In a cylindrical flask certain sample up to a height was taken and then its mass and volume were calculated.

Mass =4461 gm

Volume $=10^{-5}$

Thus bulk density =mass/volume

$=446.1\ Kg/m^3$

3.3.4. PLOTTING CALIBRATION CURVE:

Dye solutions in water were prepared with concentrations 4mg/1L, 8mg/1L, 10mg/1L and 12mg/1L and their % absorbances were found out by UV spectrophotometer(λ_{max}=618). With

these values a standard calibration curve was plotted. The equation of the curve was used to calculate the concentrations for various % absorbance.

Table3.2: calibration curve

CONC. OF DYE(mg/L)	%ABSORBANCE
2	0.34
4	0.5575
6	0.9767
8	1.2757
10	1.5436

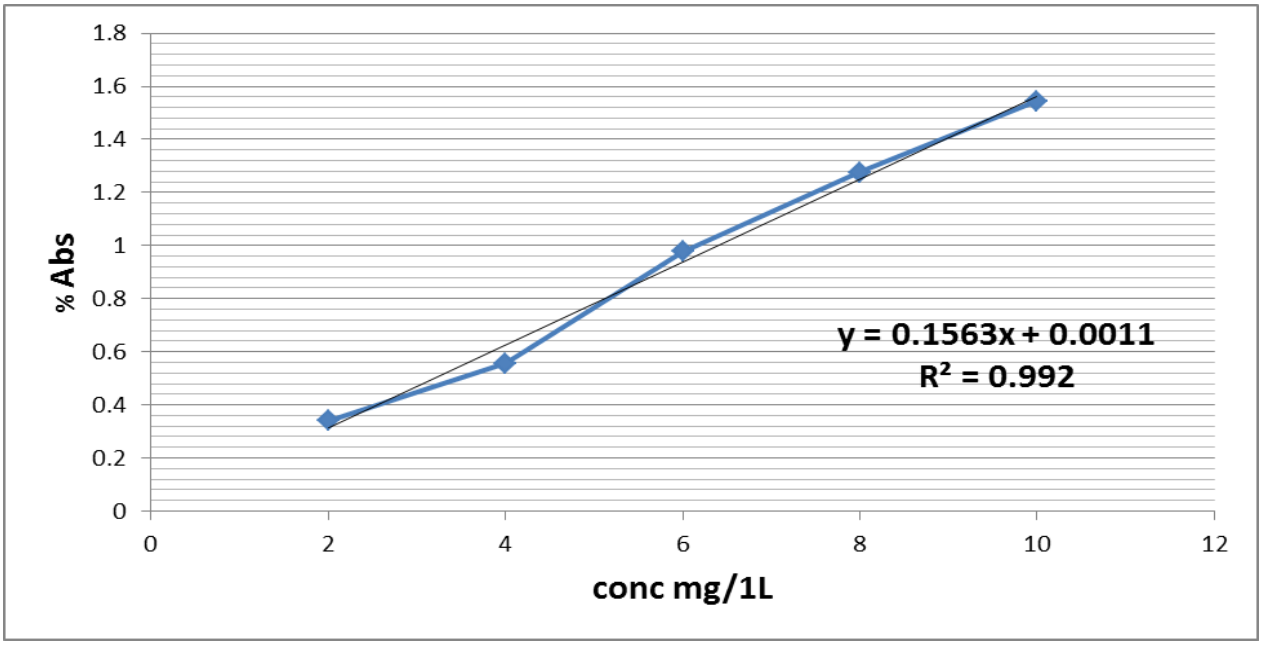


Fig: 3.8 Standard calibration curves

Equation is y= **0.1536x+.0011**

Now from this equation, concentrations can be calculated.

Where x= concentration, y=% absorbance

3.3.5. EFFECTS OF VARIOUS EXPERIMENTAL PARAMETERS:

3.3.5.1 EFFECT OF CONTACT TIME:

200 ml of dye solution with dye concentration (10mg/L) is to be prepared in a conical flask with adsorbent concentration (g/L) and kept inside the incubator shaker). The samples were withdrawn from the incubator shaker (Environmental orbital Shaker Incubator, DENEB INSTRUMENTS) at predetermined time intervals. % absorbances were estimated by using spectrophotometer (JASCO UV/Vis-550, RPM=101, temp=26^{o}C) at the wavelength corresponding to maximum absorbance, (λ_{max}=618). The dye solutions should be taken by the help of micropipettes. The dye concentrations were measured after 5, 10, 15, 20, 25, 30, 35,40,50,60, 90,105,120,135 and 150 minutes until equilibrium reached. A graph was plotted with q_e vs time [1]. The q_e is expressed as

$$qe = (C0 - C)/X$$

Where, q_e = Amount of dye adsorbed per unit mass of adsorbent (mg/g).

C_0= Initial dye concentration (mg/L).

C_e= Final dye concentration (mg/L).

Table 3.3 Effect of time on adsorption

TIME	%ABSORBANCE	(Ce)	q_t= (Co-Ce)/X
5	1.1894	7.6026	2.3974
10	1.1871	7.5879	2.4141
15	1.1707	7.283	2.517
20	1.1475	7.3346	2.6554
25	1.0690	6.832	3.168
30	1.0031	6.4107	3.5893
35	0.9101	5.8157	4.1843
40	0.8604	5.4977	4.5023
50	0.5642	3.6027	6.3973
60	0.4414	2.8170	7.1830
90	0.1733	1.017	8.9830
105	0.1299	0.824	9.1760
120	0.0887	0.5605	9.4395
135	.0670	0.4216	9.5780
150	.0340	0.2105	9.80

3.3.5.2 EFFECT OF pH

Four dye solutions of 200 ml each were prepared in conical flasks with dye conc. 10mg/L and Char conc. (g/L) and initial pH of the conical flask was measured. The pH of the dye solutions were adjusted with dilute HCl (0.1N) or KOH (0.1N) solution by using a pH meter (EUTECH Instrument, pH 510) with pH of solutions being 4,6,8,10 .The flasks were put inside the incubator shaker(101rpm fixed throughout the study, maintained at 26 ^{o}C) and the

final % absorbances of dye solutions were measured using UV spectrophotometer (λ_{max}=618). Thus the amount of dyes in different solutions left was calculated.

Table 3.4: Effect of time on adsorption percentage at pH=4.

TIME	%ABSORBANE	CONC (Ce)	q_e= (Co-Ce)/X	%ADSORBED
10	1.4470	9.25	.75	7.5
30	1.4108	9.02	.98	9.8
60	1.3852	8.85	1.15	11.5
90	1.2915	8.26	1.74	17.4
120	1.185	7.57	2.43	24.43

Table 3.5: Effect of time on adsorption percentage at pH=6.

TIME	%ABSORBANCE	C_e	$q_e=(C_o-C_e)/X$	%ADSORBED
10	1.339	8.56	1.44	14.4
30	1.2581	8.04	1.96	19.6
60	1.2123	7.75	2.25	22.5
90	1.037	6.63	3.27	32.7
120	.985	6.30	3.70	37

Table 3.6: Effect of time on adsorption percentage at pH=8.

TIME	%ABSORBANCE	C_e	q_e	%ADSORBED
10	1.2775	7.54	2.46	24.6
30	1.1059	7.07	2.93	29.3
60	1.1048	7.02	2.98	29.8
90	.9014	5.76	4.24	42.4
120	.6580	4.15	5.85	58.5

Table 3.7: Effect of time on adsorption percentage at pH=10.

TIME	%ABSORBANCE	C_e	q_e	%ADSORBED
10	.9668	6.59	3.52	35.2
30	.8732	6.48	3.41	47.3
60	.7403	4.73	5.27	52.7
90	.3220	2.053	7.95	79.5
120	.2276	1.45	8.55	85.5

3.3.5.3 EFFECT OF INITIAL CONC OF MALACHITE GREEN:

Three solutions of dye in distilled water were prepared in conical flasks with varying concentrations of dye-5mg/1L, 10mg/1L and 15mg/1L. Char was put into the solutions (with concentration 1mg/ml) and were put into the incubator shaker (RPM=101, temp=26oC) for 2 hours. Their % absorbances were determined using spectrophotometer (λmax=618) [1].

Table 3.8: Effect of time on equilibrium adsorption at 5 mg/L.

Time	%ABSORBANCE	Ce	q_e
10	.7172	4.58	5.42
30	.6472	4.13	5.87
60	.3770	2.40	7.60
90	.2810	1.79	8.21
120	.1393	.88	9.12

Table 3.9: Effect of time on equilibrium adsorption at 10 mg/L.

TIME	%ABSORBANCE	Ce	qe
10	.9208	5.88	4.12
30	.7684	4.91	5.09
60	.4240	2.70	7.30
90	.2988	1.91	8.09
120	.1657	1.05	8.96

Table 3.10: Effect of time on equilibrium adsorption at 15 mg/L.

TIME	%ABSORBANCE	Ce	qe
10	1.1752	7.51	2.49
30	.9553	6.07	3.93
60	.4769	3.04	6.96
90	.3304	2.11	7.89
120	.2087	1.33	8.67

3.3.5.4 EFFECT OF TEMP:

Three solutions of dye were prepared (dye concentration 10mg/1L and char concentration 1mg/1ml) and were put in the incubator shaker (RPM=101, temp=26^{o}C) at different temperatures – 20^{0}C, 30^{o}C and 40^{o}C for 2 hours. Their % absorbances were calculated using spectrophotometer (λmax=618) [1].

Table 3.11: Effect of time on equilibrium adsorption at 20^{o}C .

TIME	%ABSORBANCE	Ce	qe
30	1.2080	7.72	2.28
60	.510	3.20	6.8
90	.1829	1.16	8.84
120	.1028	.65	9.35

Table 3.12: Effect of time on equilibrium adsorption at 30^{o}C.

TIME	%ABSORBANCE	qe	qe
30	1.1130	7.11	2.89
60	.4568	2.92	7.08
90	.1693	1.07	8.93
120	.088	.56	9.44

Table 3.13: Effect of time on equilibrium adsorption at 40^{o}C.

TIME	%ABSORBANCE	Ce	qe
30	1.032	6.6	3.4
60	.4328	2.76	7.24
90	.1449	.92	9.08
120	.067	.42	9.58

3.3.5.5 EFFECT OF ADSORBENT DOSE

Adsorbent dose effect was studied by preparing 5 different solutions of dye and char in distilled water in different conical flasks with constant concentration of malachite green dye and varying dose of char 40mgg/100ml, 60mg/100ml, 80mg/100ml, 100mg/100ml, 150mg/100ml. These solutions were prepared in 200 ml conical flasks and put in the incubator shaker (RPM=101, temp=26^{o}C) for 2 hours. Then their % absorbances were calculated by spectrophotometer (λ_{max}=618). And thus amount adsorbed were calculated.

Table 3.14: Effect of adsorbate dose on equilibrium adsorption.

CHAR CONC(MG/100ML)	%ABSORBANCE	Ce	Qe
40	.8622	5.51	4.49
60	..6108	3.90	6.10
80	.3940	2.51	7.49
100	.2719	1.73	8.27
150	.2487	1.58	8.42

3.3.6 ADSORPTION KINETICS:

Dye solution was prepared in a conical flask with dye concentration 10mg/1L and char concentration 1mg/ml. The flask was put in the incubator shaker (RPM=101, temp=26^{o}C) for two and half hours. Samples were collected with different time periods and their % absorbances were determined using spectrophotometer (λ_{max}=618). These values were used to calculate q_t (amount of dye adsorbed per unit amount of char) values at different time, the q_t for equilibrium time (150min) was taken to be q_e. Thus using equations for pseudo first order and second order kinetic model we determine the best fitting kinetic model for the system [1].

Table 3.15: Adsorption kinetics study

TIME	%ABSORBANCE	(Ce)	q_t= (Co-Ce)/X
5	1.1894	7.6026	2.3974
10	1.1871	7.5879	2.4141
15	1.1707	7.283	2.517
20	1.1475	7.3346	2.6554
25	1.0690	6.832	3.168
30	1.0031	6.4107	3.5893
35	0.9101	5.8157	4.1843
40	0.8604	5.4977	4.5023
50	0.5642	3.6027	6.3973
60	0.4414	2.8170	7.1830
90	0.1733	1.017	8.9830
105	0.1299	0.824	9.1760
120	0.0887	0.5605	9.4395
135	.0670	0.4216	9.5780
150	.0340	0.2105	9.80

Pseudo-first-order kinetic model is given by

$$\frac{dq}{dt} = k_1 * (q_e - q_t)$$

after integration we get;

$$\ln(q_e - q_{t)} = lnq_e - k_1 * t$$

where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively. k_1 is the rate constant.

The curves are plotted for pseudo-1st-order

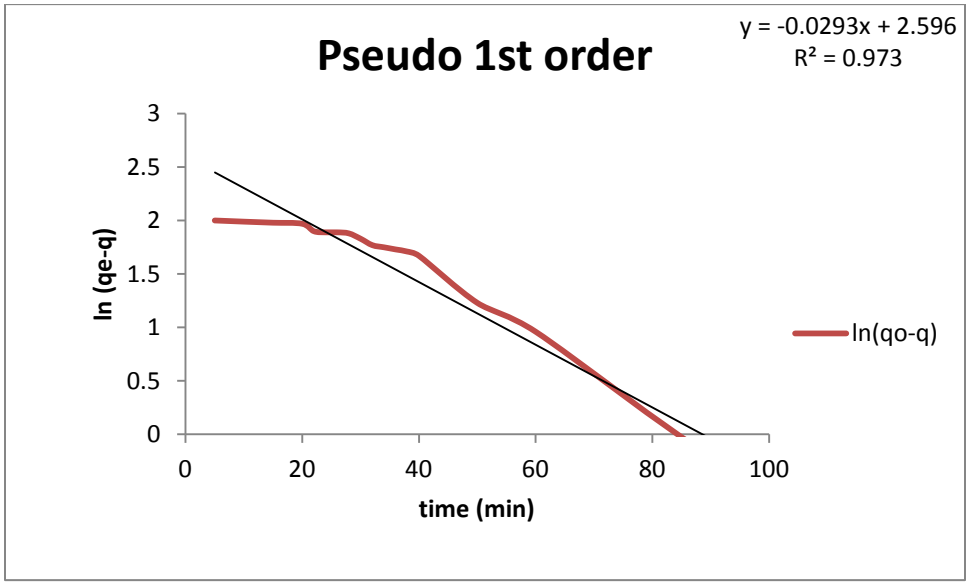


Fig 3.9: Pseudo 1st order curve.

Slope gives $k_1$and intercept gives q_e.

Table 3.16: Parameters of pseudo 1st order

Co (mg/L)	**$Q_{e,exp}$ (mg/g)**	**$Q_{e,cal}$(mg/g)**	**k_1(1/min)**	**R^2**
10	9.8	13.40	.029	.973

Pseudo-second-order kinetic model is given by

$$\frac{dq}{dt} = k_2 * (q_e - q_t)^2$$

after integration,

$$\frac{t}{q_t} = \frac{1}{k_2 * {q_e}^2} + \frac{t}{q_e}$$

where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively.k_2 is the rate constant.

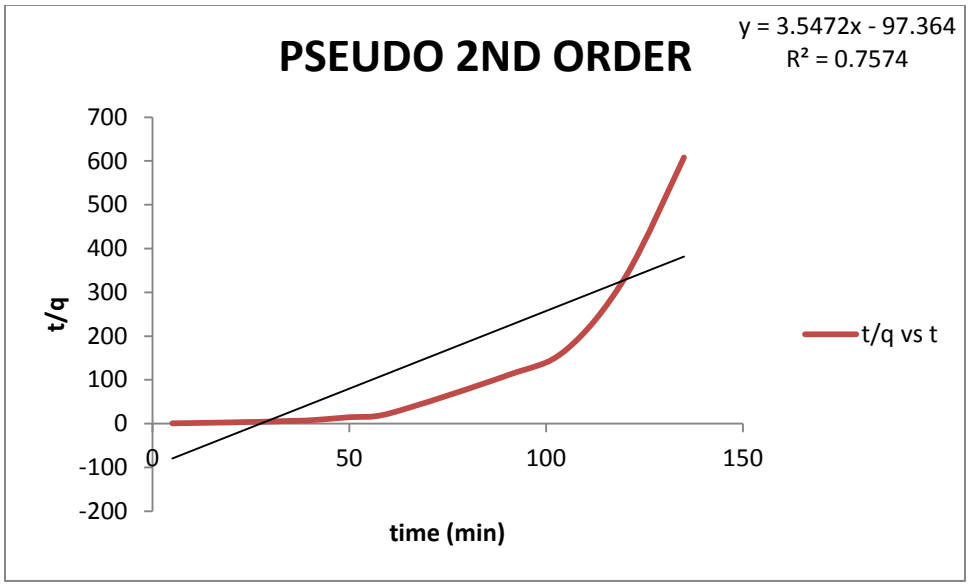


Fig 3.10:Pseudo-second order study.

Slope gives q_e and intercept gives k_2.

Table 3.17: Experimental parameters for pseudo 2nd order

Co (mg/L)	Qe,exp (mg/g)	Qe,cal(mg/g)	K2(1/min)	R2
10	9.8	.25	-.164	.752

3.3.7 ADSORPTION ISOTHERMS

Dye solutions were prepared for three different initial pHs namely 4, 7 and 10. The dye concentrations were varied such as 25mg/L, 50mg/L, 75mg/L and 100 mg/L keeping the char

concentrations constant 1mg/ml. All these twelve solutions in the conical flasks were kept in the incubator shaker (RPM=101, temp=26oC) for two hours. Their % absorbances were determined using spectrophotometer (λmax=618). These values were used to calculate Ce and qe values. With these values we plot curves for Freundlich, Langmuir and Temkin isotherms and we determine the best fitting model.

Table 3.18: Effect of different initial concentration of MG adsorption at pH-4

CONC	**Ce**	**q_e**	**lnqe**	**lnc_e**	**$1/c_e$**	**$1/q_e$**
25	11.07	14	**2.63**	**2.4**	.091	.071
50	15.94	34	**3.53**	**2.77**	.063	.029
75	20.99	54	**3.98**	**3.04**	.048	.018
100	25.5	75.5	**4.32**	**3.24**	.039	.013

Table 3.19. Effect of different initial concentration of MG adsorption at pH-7

CONC	**Ce**	**qe**	**lnCe**	**lnqe**	**1/Ce**	**1/qe**
25	8.67	16.33	2.16	2.79	.115	.061
50	15.92	34.08	2.75	3.53	.063	.029
75	18.39	56.61	2.91	4.02	.054	.017
100	19.27	80.73	2.96	4.39	.052	.012

Table 3.20: Effect of different initial concentration oF MG adsorption, pH10

CONC	**Ce**	**qe**	**lnCe**	**lnqe**	**1/Ce**	**1/qe**
25	7.177	17.82	1.97	2.88	.139	.056
50	13.03	36.97	2.56	3.61	.077	.027
75	15.44	59.56	2.73	4.08	.065	.016
100	18.61	81.40	2.92	4.39	.054	.012

Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{b * q_0 * C_e} + \frac{1}{q_0}$$

A curve $1/q_e$ vs $1/Ce$ is plotted, the intercept gives the qo value and slope gives the k_L value

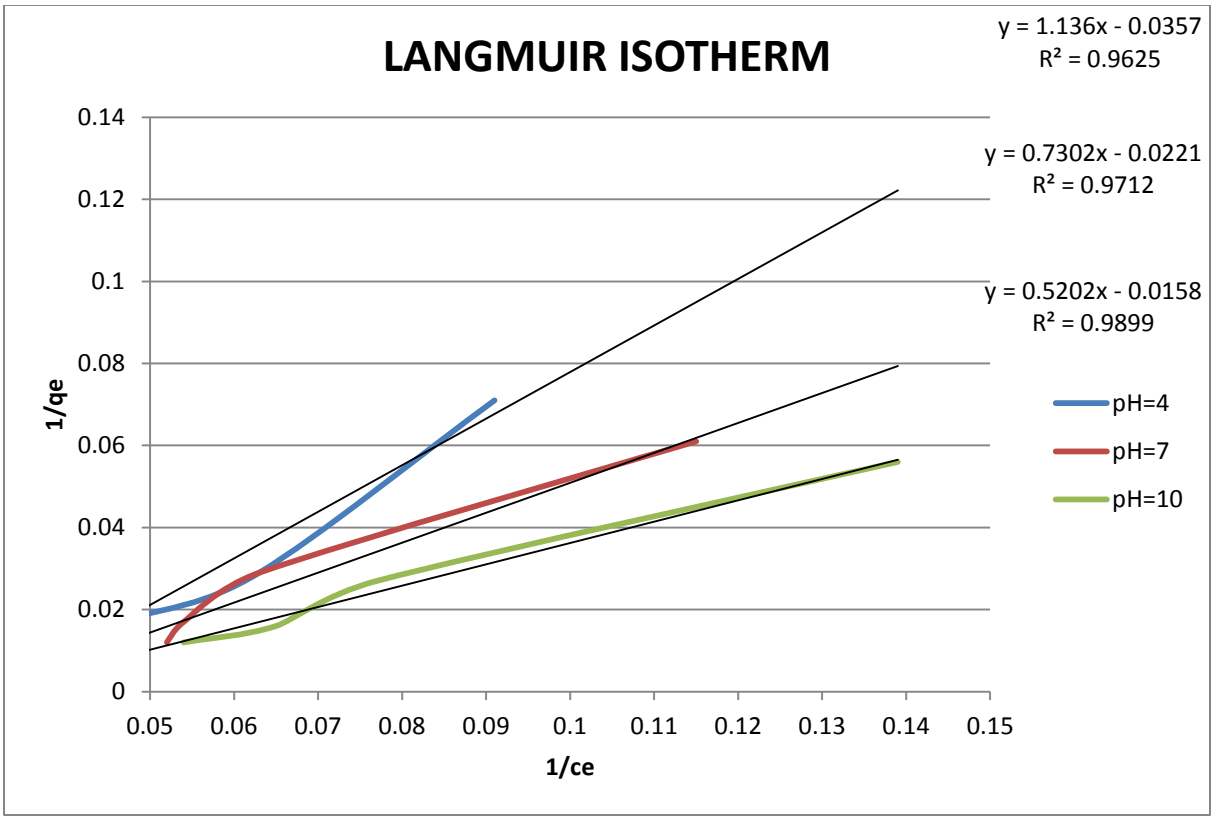


Fig: 3.11 Langmuir isotherm curve.

Freundlich isotherm model:

$$\ln q_e = lnk_f + \frac{1}{n * lnC_e}$$

A curve $\ln(q_e)$ vs $\ln(C_e)$is plotted , the slope gives 'n' value and intercept gives K_f value.

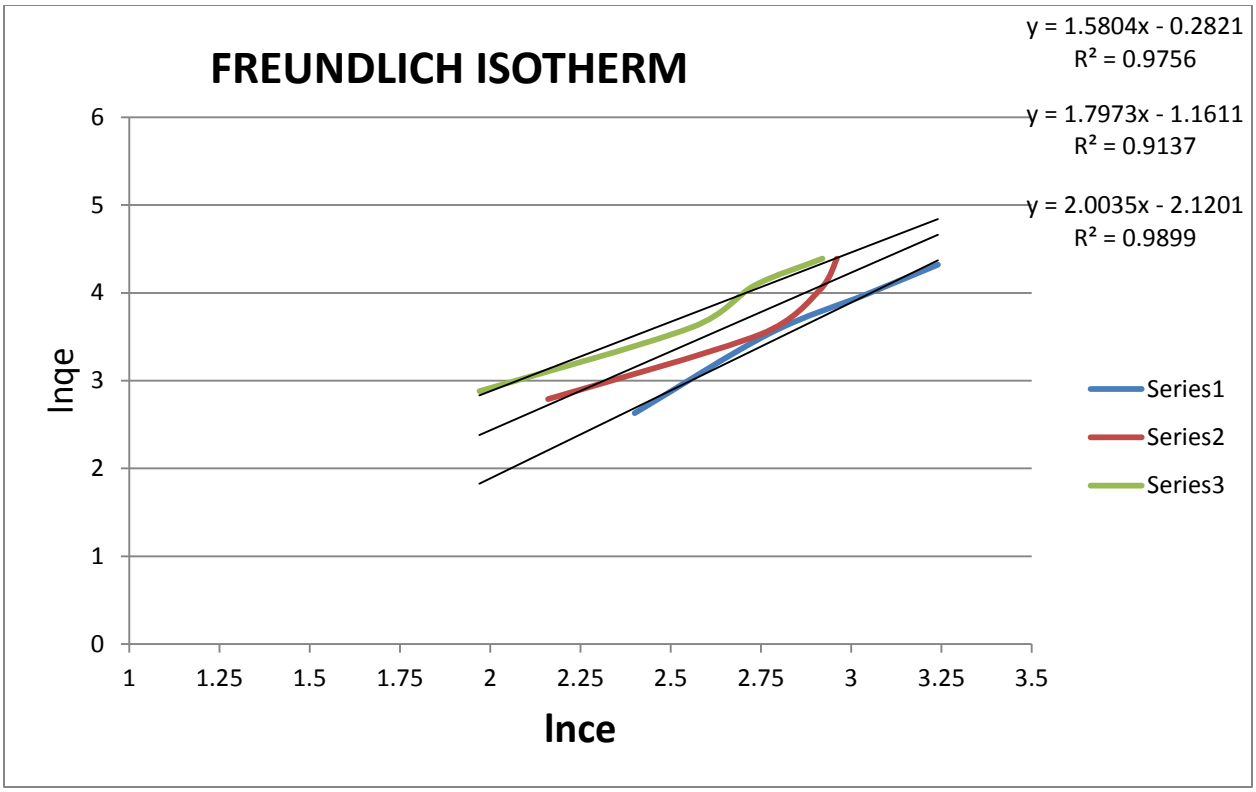


Fig 3.12: Freundlich isotherm curve

Temkin model:

qe = BlnA + BlnCe [10]

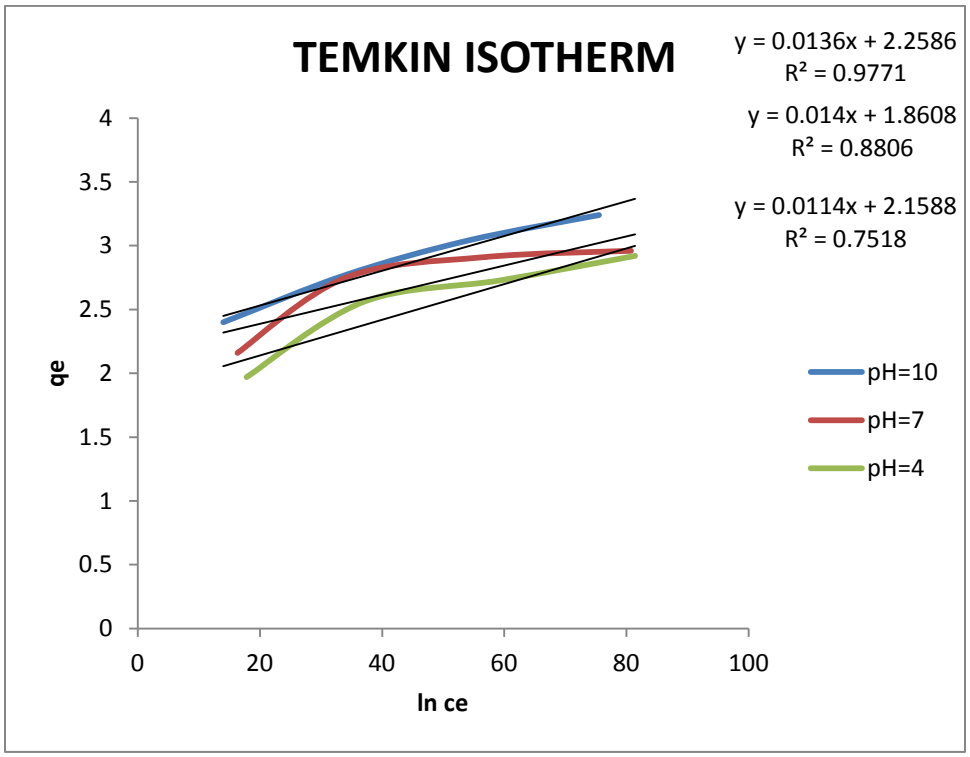


Fig:3.13: Temkin isotherm

CHAPTER-4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1 PROXIMATE ANALYSIS:

Proximate analysis was performed for char to know its different characteristics and carbon content. It shows very less moisture content and volatile matter and ash contents are also not very large. The carbon content is reasonably good enough to make Sheesham seeds char act as a good low-cost adsorbent.

Table 4.1: Proximate analysis results.

CONTENT	%AGE
%MOISTURE CONTENT	3
%VOLATILE MATTER	38.1
%ASH CONTENT	24.5
%CARBON	34.4

4.2 ZETA POTENTIAL:

It indicates the surface potential of material and it was -56.4 mV which shows that the surface of the char is negatively charged. The negative charges on the surface increases the adsorption as malachite green is a cationic dye. Zeta potential in the range of 40-60 shows stability of material as high zeta potential indicates that flocculation of materials don't take place.

Table 4.2: Zeta potential

ZETA POTENTIAL(mV)	-56.4
ZETA DEVIATION (mV)	10.7
RESULT QUALITY	GOOD

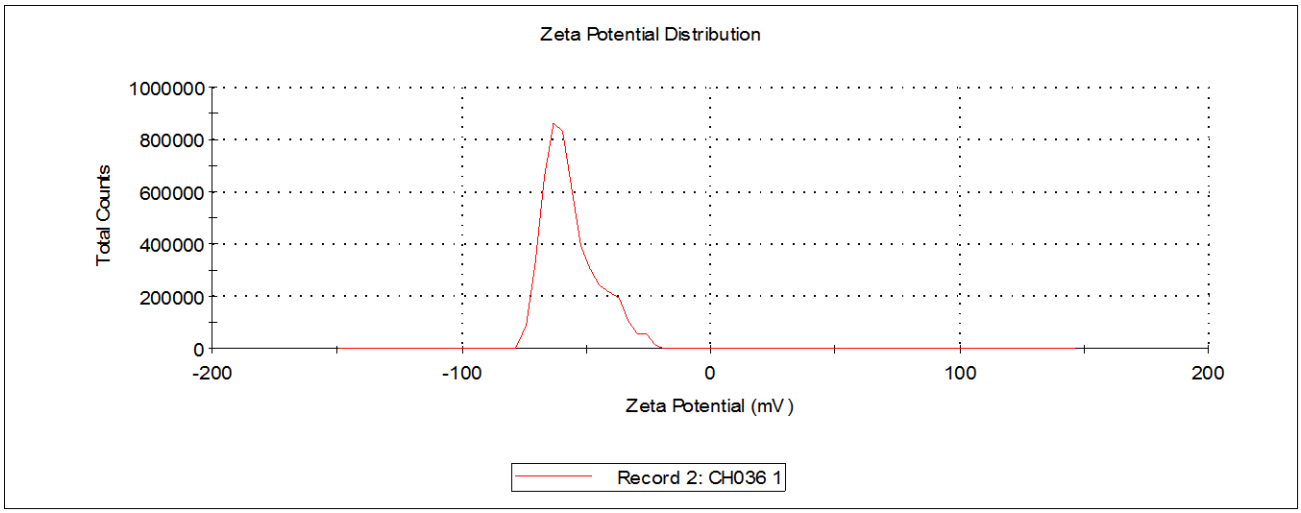


Fig 4.1: Zeta potential curve

4.3 FTIR

Infrared spectroscopy is a useful tool for identifying the functional groups present and for obtaining information on the nature of possible interactions between adsorbent and adsorbate. FTIR shows the change in properties of the surface on addition of malachite green dye.

BEFORE ADSORPTION FUNCTIONAL GROUPS PRESENT:

Alkyl C-H Stretch
Carboxylic Acid O-H Stretch
Ketone C=O Stretch
Aromatic C=C Bending
Aromatic C=C Bending
NO_2 (aromatic)
C-O stretch, carboxylic acids
phosphine oxides

AFTER ADSORPTION FUNCTIONAL GROUPS PRESENT:

Alkenyl C-H Stretch
Phosphines P-H stretch
Anhydrides C=O stretch
Amides N-H stretch
carboxylic acids O-H stretch
nitro groups NO_2 (aliphatic)
phosphine oxides P=O
Aromatics C-H bend (para)

BEFORE ADSORPTION

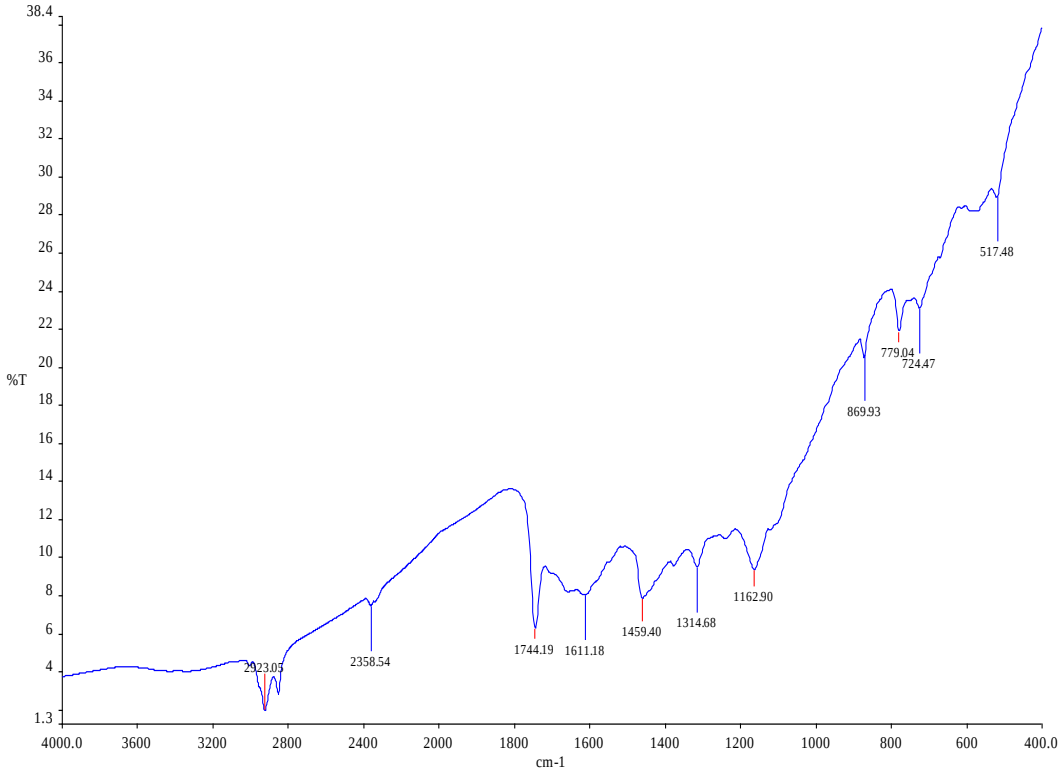


FIG 4.2: FTIR spectra for char before adsorption

AFTER ADSORPTION

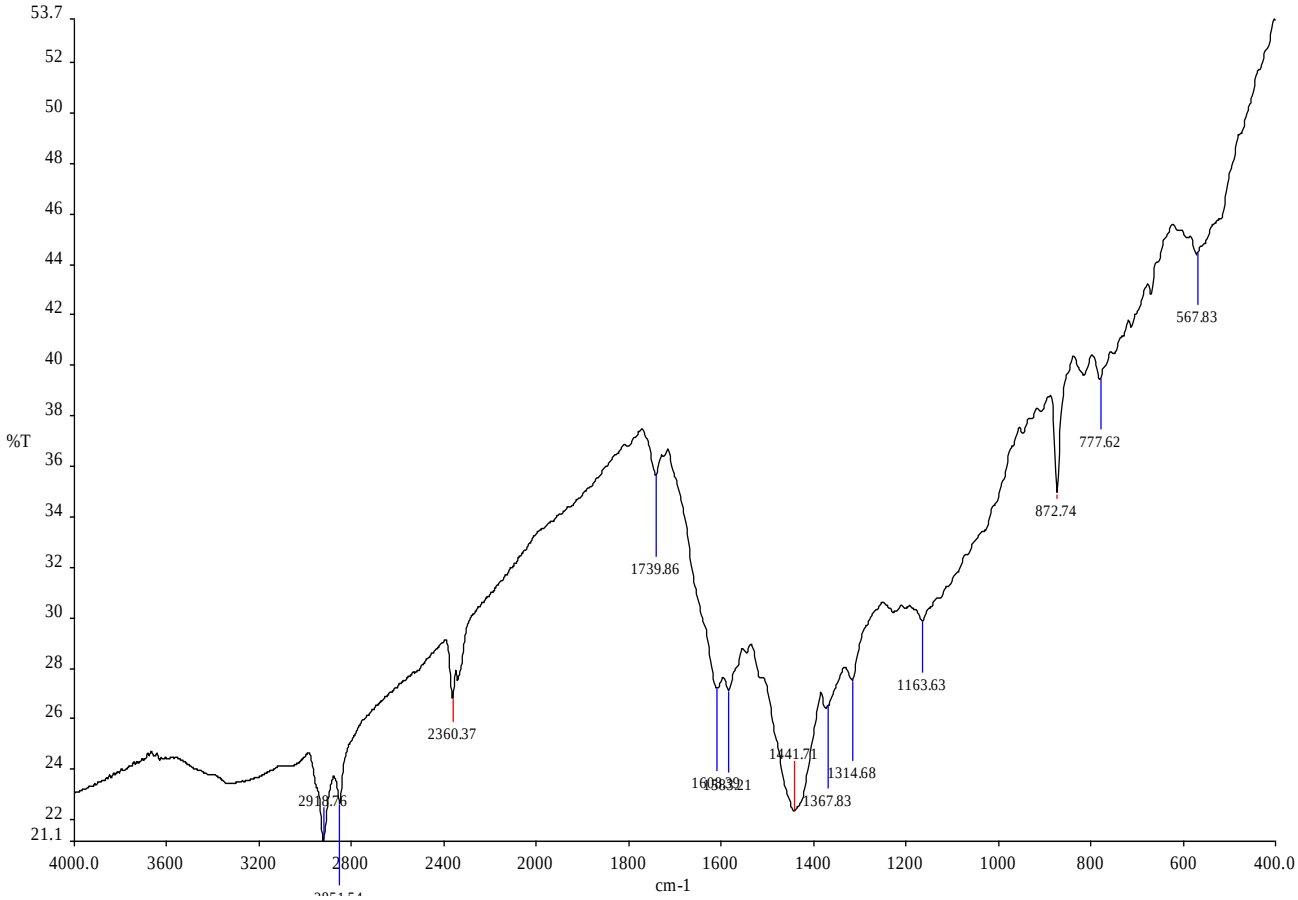


Fig 4.3: FTIR spectra for char after adsorption

4.4. CALIBRATION PLOT:

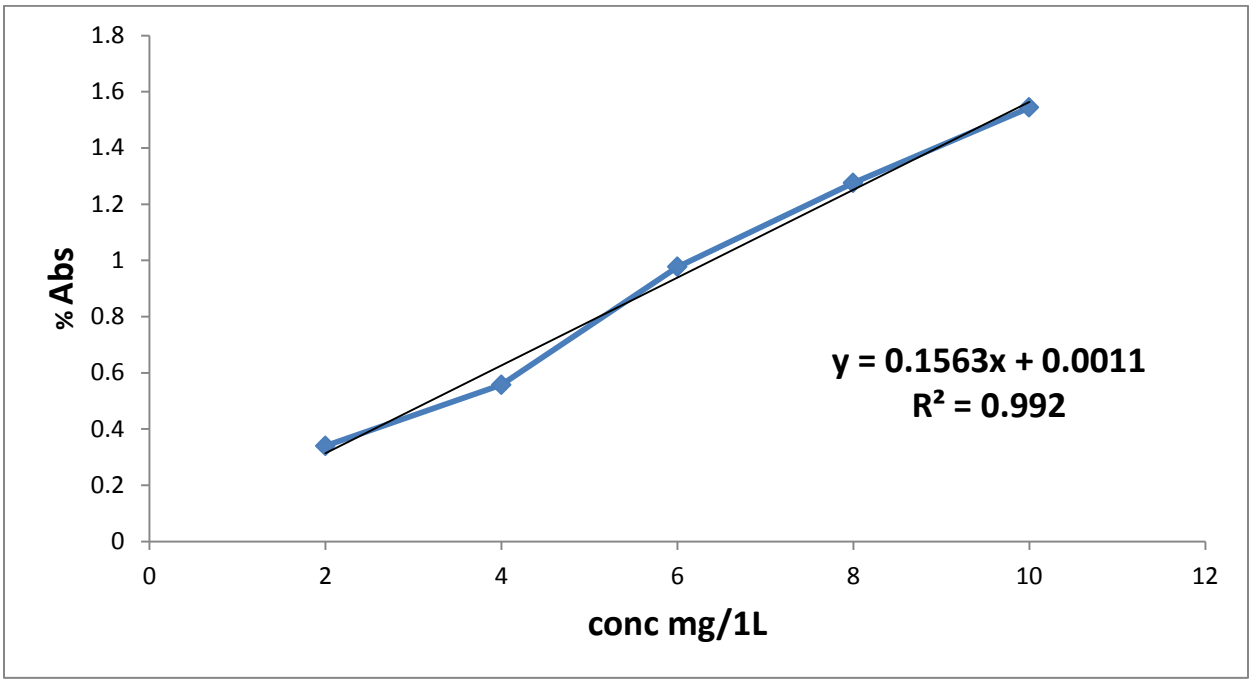


Fig 4.4: Calibration plot

4.5 ADSORPTION STUDIES:

4.5.1 EFFECT OF CONTACT TIME:

The effect of contact time can be seen from Fig.4.1.2 for the dyes. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 2 hours from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 2 hours (120 min). It is basically due to saturation of the active site which do not allow further adsorption to take place [4,10,11].

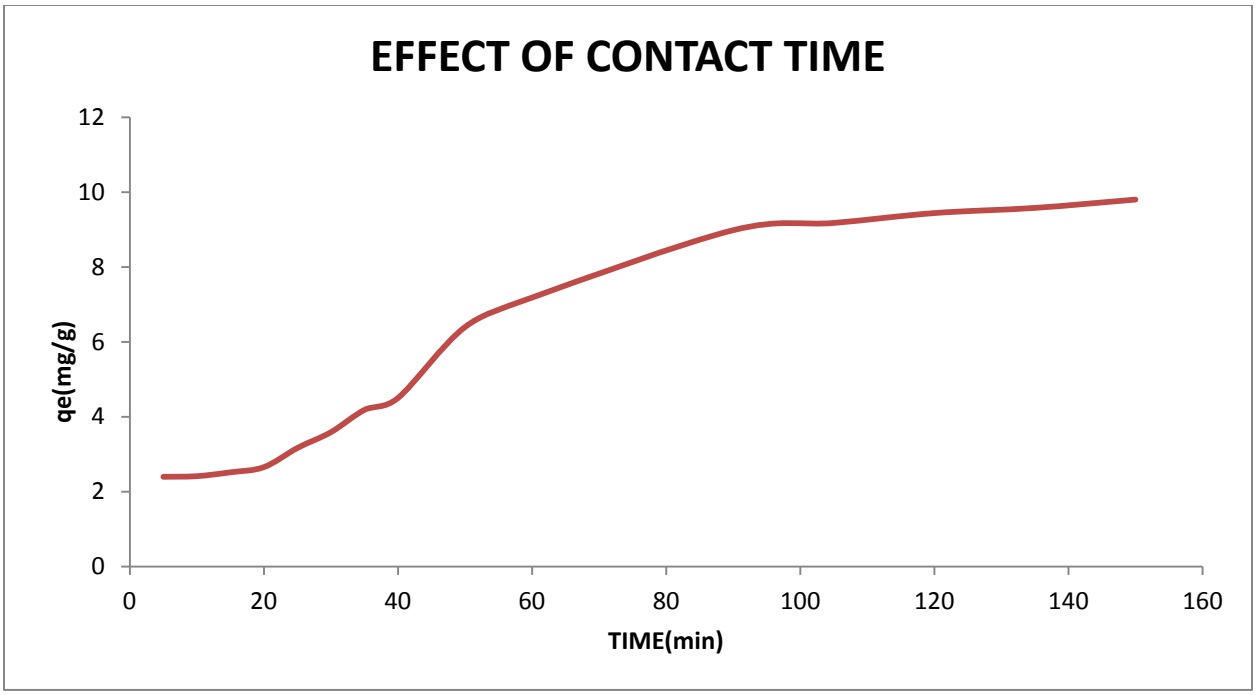


Fig 4.5 Effect of contact time

4.5.2 EFFECT OF INITIAL pH OF SOLUTION

The effects of initial pH on dye solution of three dyes removal were investigated by varying the pHs 4, 6,8,10. At pH - 4 the removal was found to be minimum and it increased as initial pH of dye solutions were increased. It was maximum at pH = 10 as we see in the graph of q_e Vs time. Sometimes adsorption is found to decrease with increase in pH of solution [1]. The adsorption of these positively charged dye groups on the adsorbent surface is mainly influenced by the surface charges on the adsorbent which in turn is influenced by the pH of the solution [1, 4, and 11]. The results showed that availability of negatively charged groups at the adsorbent surface are necessary for the adsorption of basic dyes to proceed which we see at pH 4 is almost unlikely as there would accumulation of net positive charge in the adsorption system due to the presence of H30+[1,2,11,17]. With increase in negative charges on the surface, adsorption of malachite green dye which is a cationic dye would obviously increase. Thus as the pH increased, more negatively charged surface was available thus increasing the dye removal [2, 16, 18]

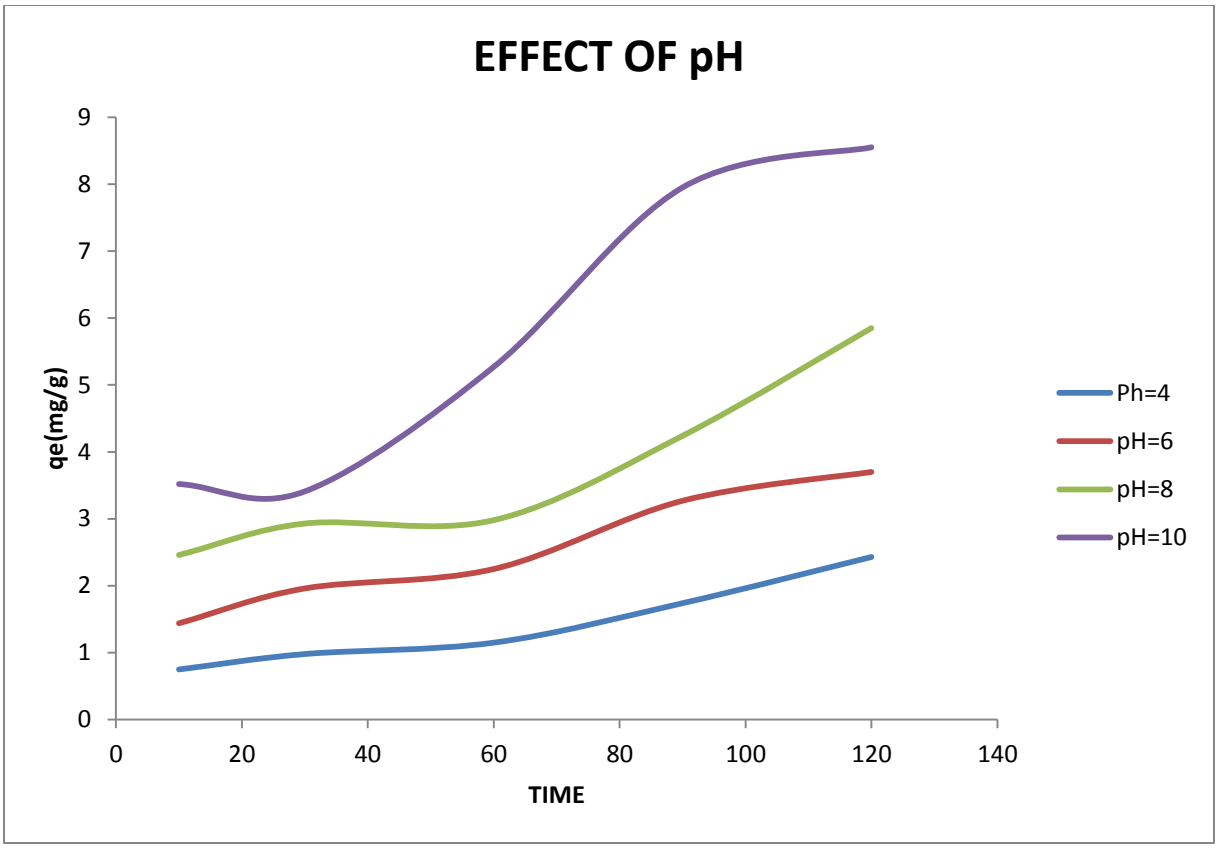


Fig 4.6: Effect of pH

4.5.3 EFFECT OF INITIAL CONCENTRATION OF MALACHITE GREEN:

Results show that with increase in adsorbate dose adsorption increases, optimum dose for the dye being 10g/1L. Though we find that at 15mg/1L, there is a slight increase in qe value but this is nearly the same as we get in 10 mg/1L adsorbent dosage so going for 15mg/1L will only be expensive and loss of adsorbent. The decreasing increment in adsorption capacity with an increase in the adsorbate concentration could be explained by the fact that some of the adsorption sites remains unsaturated during the process as the adsorbate quantity are more as compared to the adsorbent dosage [4,11,16].

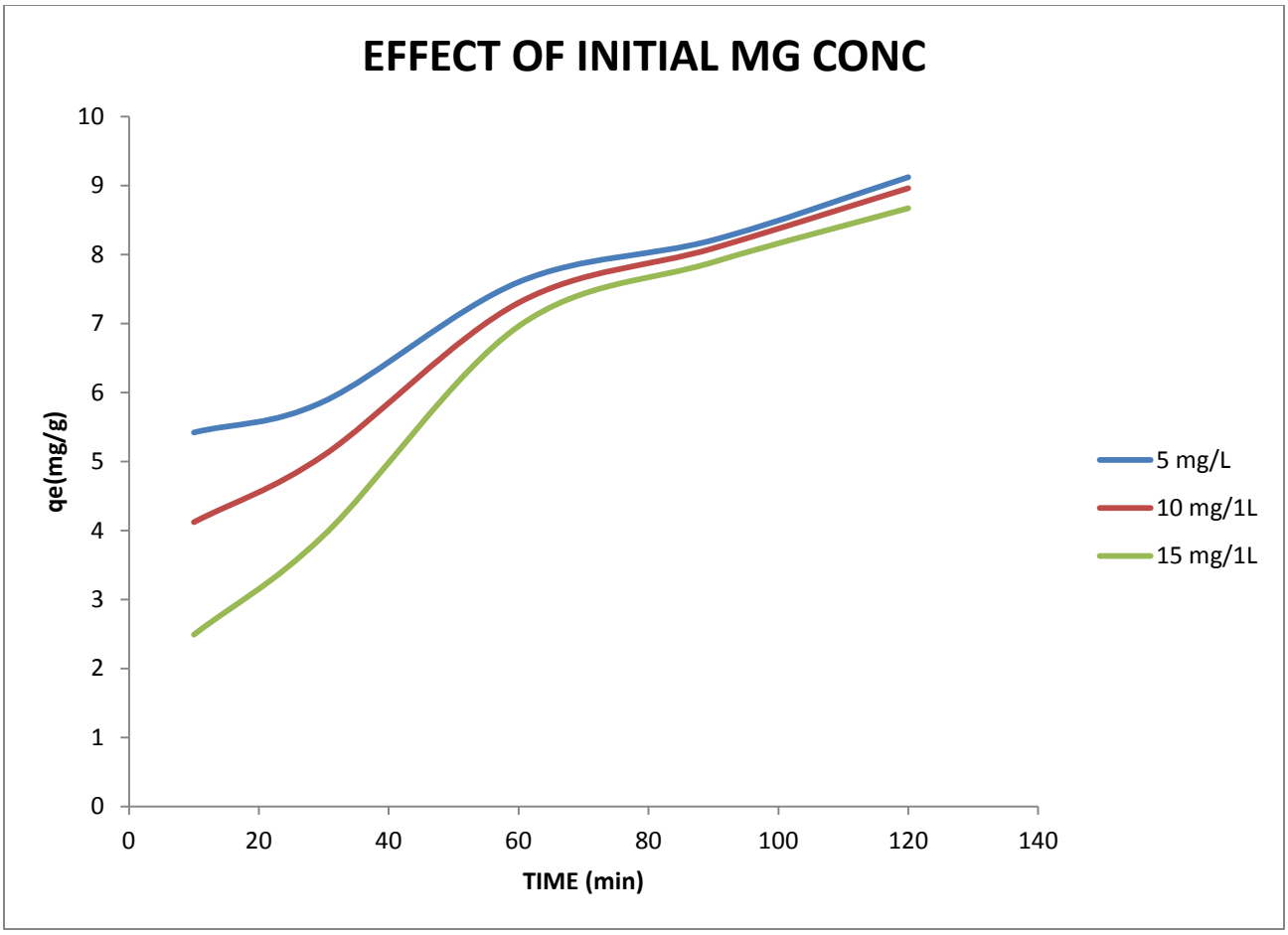


Fig 4.7: Effect of initial conc. of MG

4.5.4 EFFECT OF TEMPERATURE

The effect of temperature on removal of dye solution was studied with initial concentration of malachite green =10mg/1L and char concentration 1g/1L at pH=solution pH the temperatures were varied in the range of 20, 30 and 40°C. The results indicated that the adsorption capacity increases with increase in temperature. This can be ascribed by the fact that with increase in temperature there is increase in the mobility of the large dye ions [11,16]. The molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Further increasing the temperature may produce a swelling effect within the internal structure of the char enabling large malachite green dyes to penetrate further into it. The result implies that chemical adsorption mechanism may play an important role in this system [4,11,16].

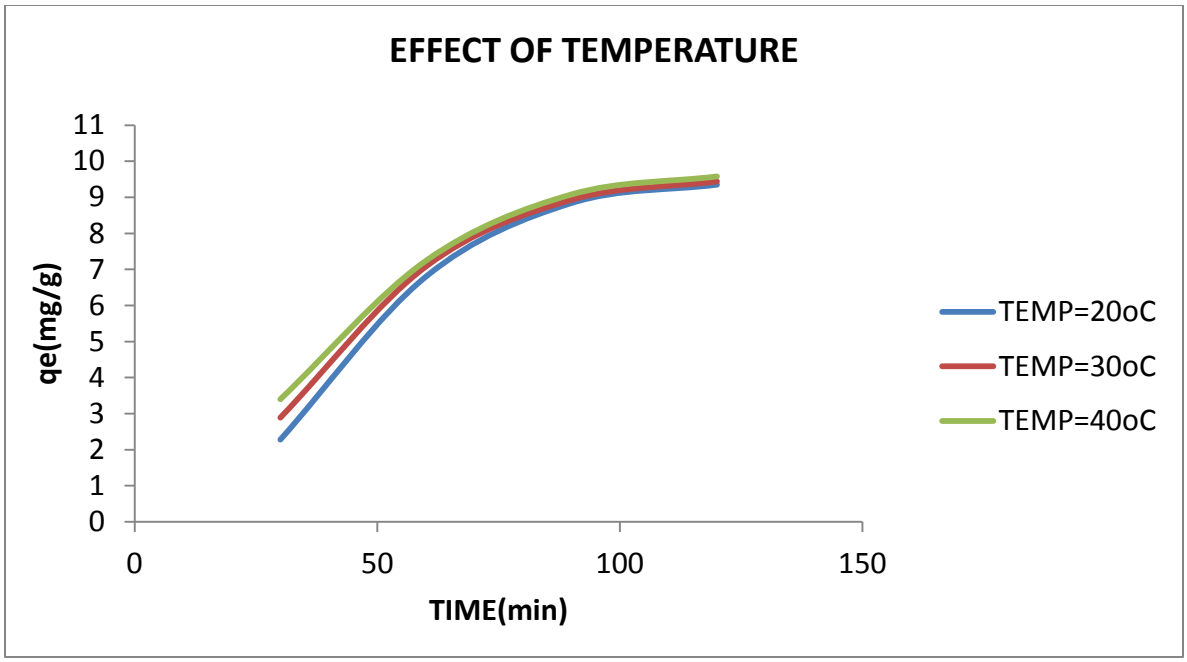


Fig 4.8: Effect of temperature

4.5.5 EFFECT OF ADSORBENT DOSE:

Effect of adsorbent dose was studied with adsorbent dose varying in the range of 40 mg/100ml, 60mg/100ml, 80mg/100ml, 100mg/100ml and 150 mg/100ml. We take 100mg/100ml as the optimum dose of adsorbent as with concentration 150mg/100ml we find nearly same adsorption so using this dose will only be cost inefficient and loss of char [11].

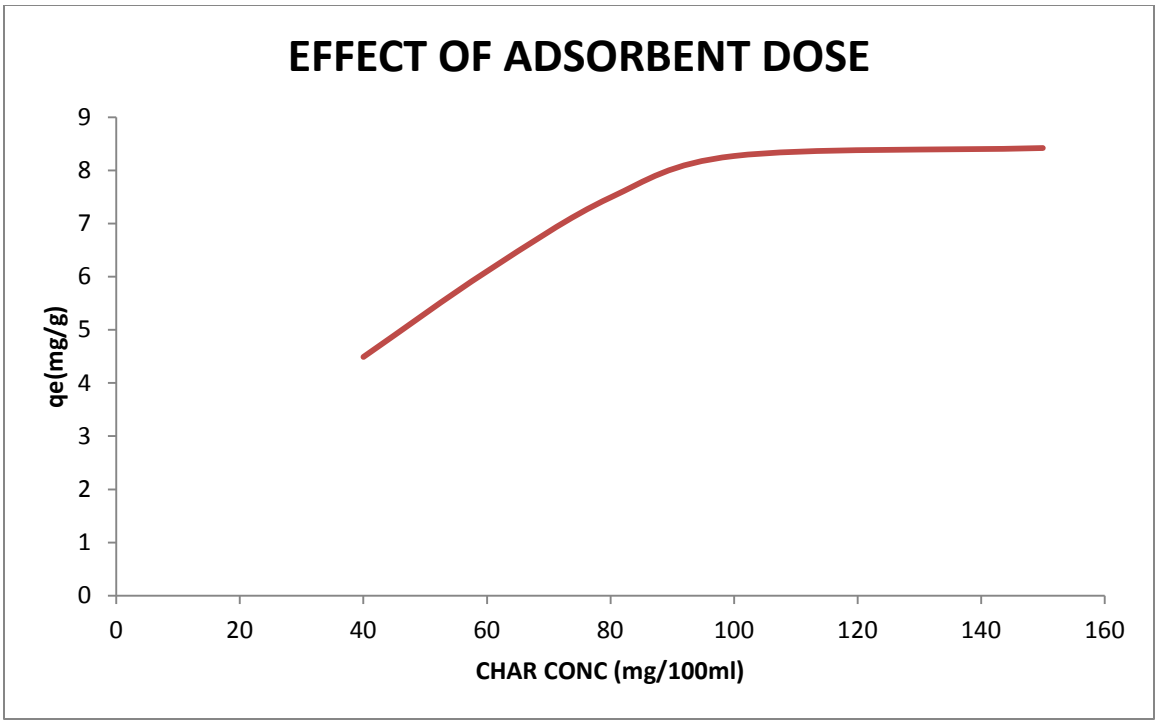


Fig 4.9: Effect of adsorbent dose

4.6 ADSORPTION KINETICS.

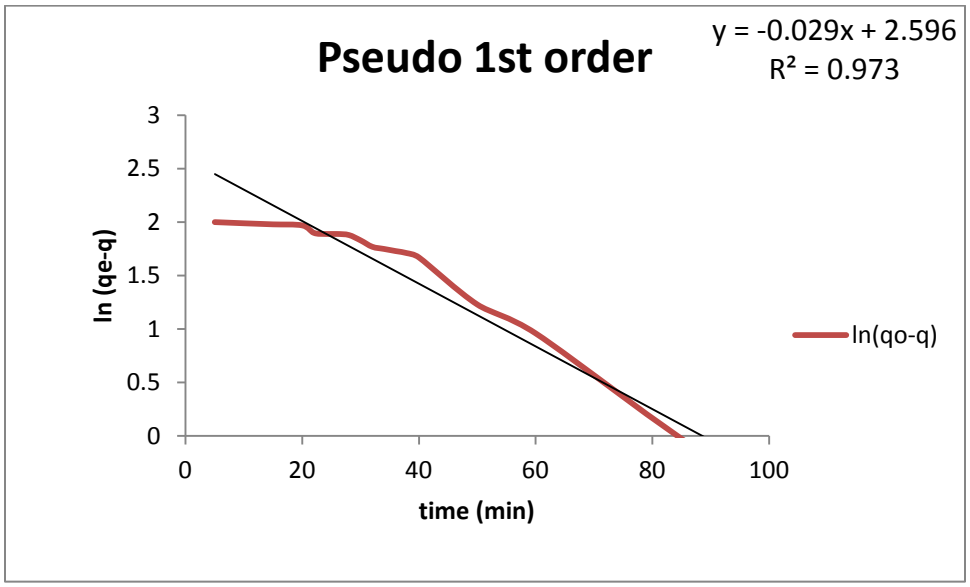


Fig 4.10: pseudo 1st order curve

Table 4.3: pseudo 1st order parameters

Co (mg/L)	Qe,exp (mg/g)	Qe,cal(mg/g)	K1(1/min)	R2
10	9.8	13.40	.029	.973

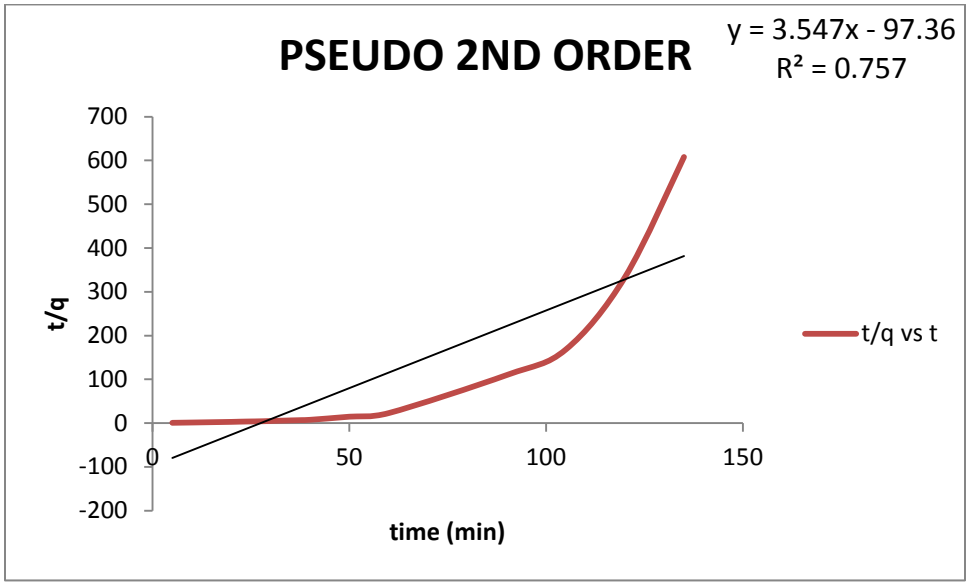


Fig 4.11 Pseudo 2nd order curve

Table 4.4: Pseudo 2nd order parameters

Co (mg/L)	Qe,exp (mg/g)	Qe,cal(mg/g)	K_2(1/min)	R^2
10	9.8	.25	.164	.752

We observe that for first order equation q_e value calculated corresponds well with the experimental value; also the R2 value is very high. For the second order q_e value calculated differs very much from the experimental value. The R2 value is also very less as compared to the

pseudo-first-order model. Thus we conclude that pseudo-first-order is the best fitting kinetic model.

4.7 ADSORPTION ISOTHERM MODELS

LANGMUIR ISOTHERM CURVE

$$\frac{1}{q_e} = \frac{1}{b * q_0 * C_e} + \frac{1}{q_0}$$

A curve $1/q_e$ vs $1/C_e$ is plotted, the intercept gives the q_o value and slope gives the k_l value

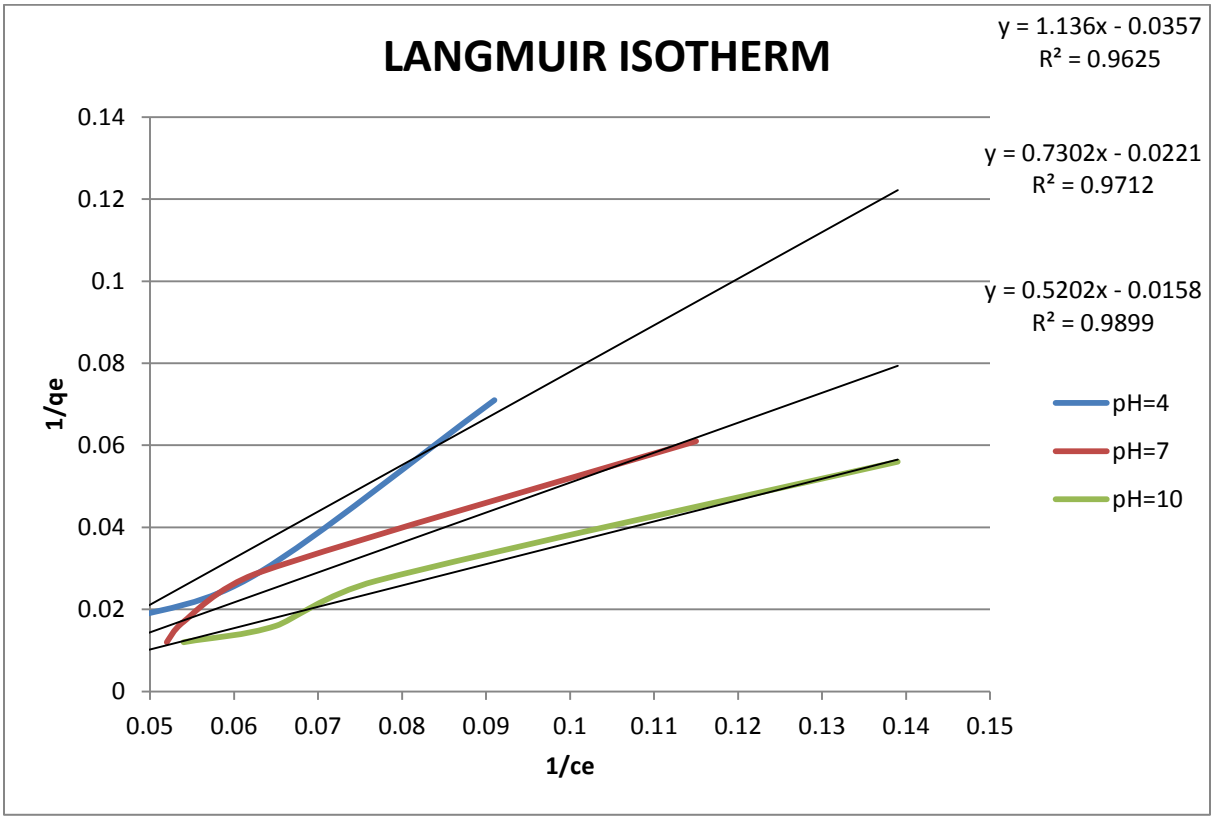


Fig 4.12: Langmuir isotherm curve

Freundlich isotherm model:

$$\ln q_e = lnk_f + \frac{1}{n * lnC_e}$$

A curve ln(qe) vs ln(Ce)is plotted , the slope gives ‘n’ value and intercept gives Kf value.

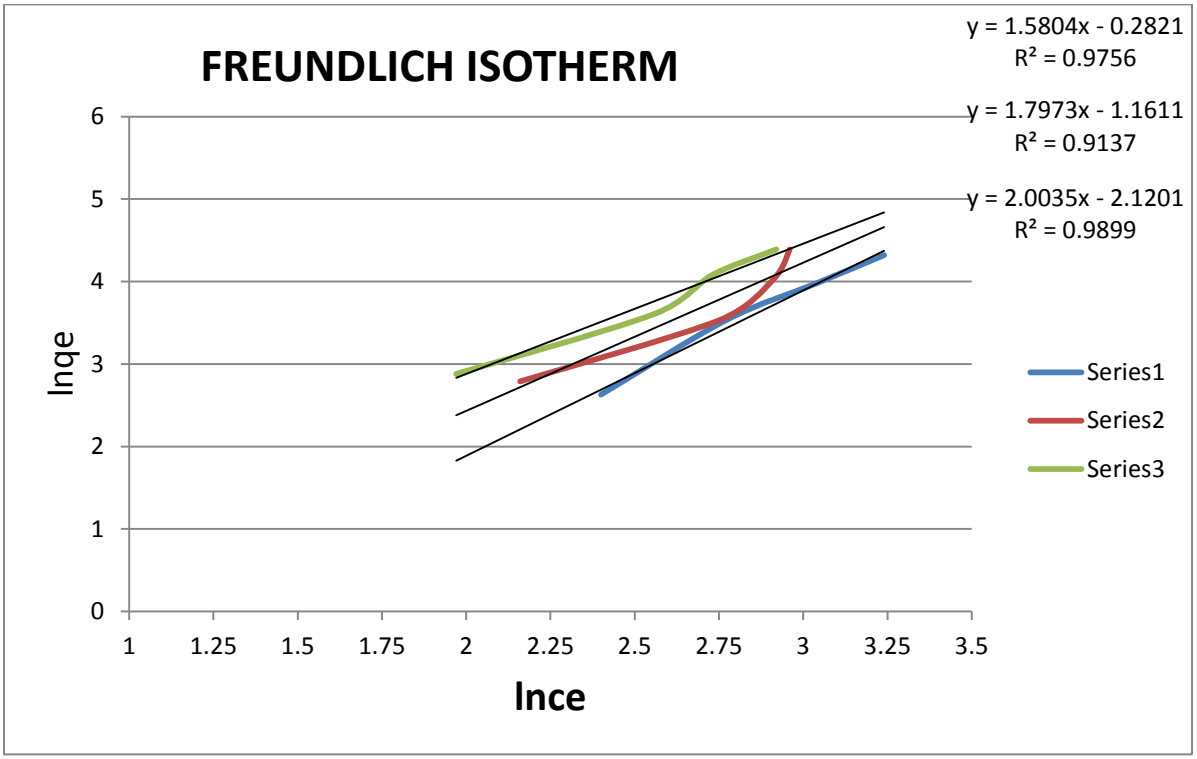


Fig 4.13: Freundlich isotherm

TEMKIN ISOTHERM MODEL:

qe = BlnA + BlnCe [10]

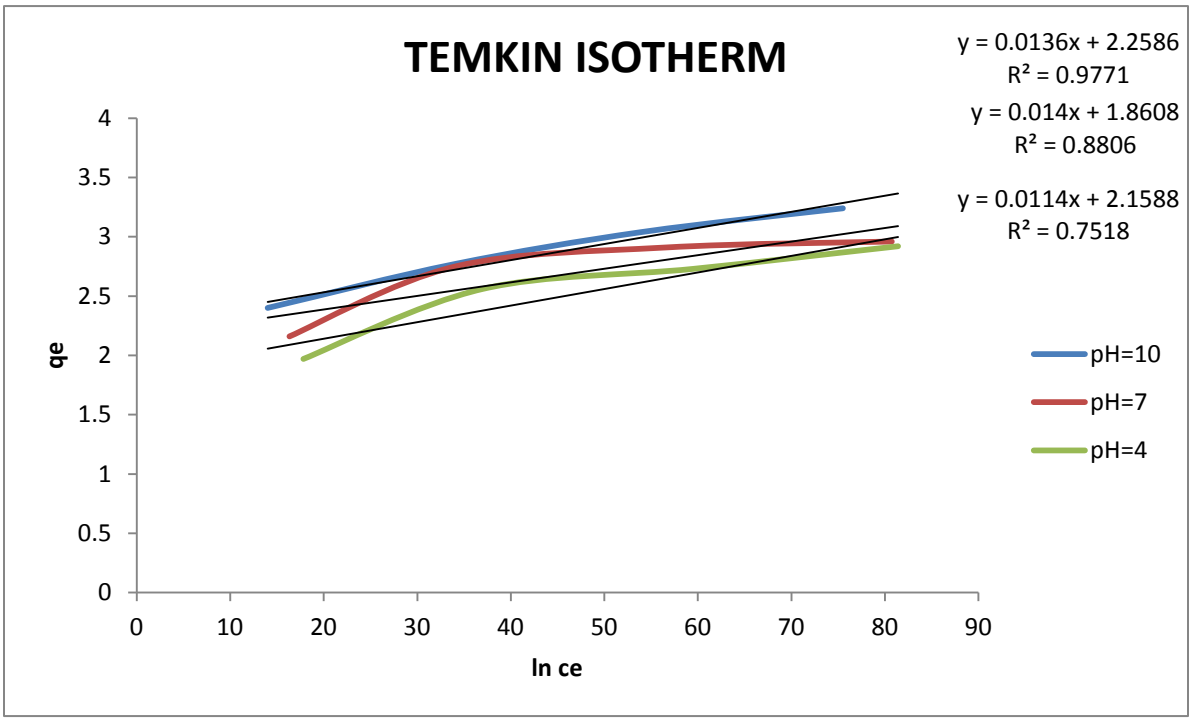


Fig 4.14: Temkin isotherm model

Table 4.5: Langmuir, Freundlich and Temkin parameters.

		pH=4	pH=7	Ph=10
LANGMUIR ISOTHERM	**KL**	**.0308**	**.031**	**.029**
	Qo	**28.57**	**45.45**	**66.66**
	R^2	**.962**	**.971**	**.989**
FREUNDLICH ISOTHERM	**KF**	**.45**	**.7**	**.33**
	n	**.63**	**.56**	**.5**
	R^2	**.913**	**.975**	**.989**
TEMKIN ISOTHERM	**B**	**218060**	**177563**	**1182785**
	A	**1**	**1**	**1**
	R^2	**.9771**	**.8806**	**.7518**

We observe that both isotherm curves fit well with the adsorption system as their R2 values are quite near and both gives reasonable values of rate constants.

Comparison :

Langmuir isotherm

Table 4.6: Comparison of isotherm parameters of different adsorption processes Langmuir isotherm.

SAMPLE	kL	q_0	R^2
Sheesham seeds char	.029	66.66	.9889
Rambutan peel based activated carbon	.036	388	.961
Ground palm kernel coat	.273	277	.9868

Freundlich isotherm

Table 4.7: Comparison of isotherm parameters of different adsorption processes for Freundlich isotherm .

SAMPLE	n	k_f	R^2
Sheesham seeds char	.5	.33	.9889
Rambutan peel based activated carbon	2.087	4.4	.977
Ground palm kernel coat	1.87	55.3	.8937

So, we see that char from sheesham seeds are at par with other low-cost adsorbents.

CHAPTER-5

CONCLUSION

5. CONCLUSIONS:

Removal of malachite green dye from aqueous solution by adsorption with char from sheesham seeds has been experimentally determined and the following observations are made:

1. Proximate analysis showed good carbon content which favors adsorption. %carbon was found to be 34.4%.The moisture content(3%), volatile content and ash content were also found to be quite reasonable.

2. Zeta potential was found to be -56.4 mV which indicates negative charge on the surface of char. It indicates that char is stable in aqueous solutions. It improves the adsorption with malachite green being a cationic dye.

3. FT-IR spectra show little change in the surface properties of char after adsorption as compared to that of before adsorption.

4. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be two hours.

5. As adsorbate dose increases there is increase in adsorption as more the adsorbate concentration more is the adsorption. Optimum dose is taken to be 10 mg/L.

6. Adsorption increases with increase in pH. The adsorption of cationic dye is mainly influenced by the amount of negative charges in the solution which is actually influenced by the solution pH. At pH=4 there is net positive charge in the solution so adsorption is less whereas at pH=10 there is increase in negative charges increasing adsorption of malachite green. Maximum adsorption was found to take place at pH=10.

7. Adsorption capacity is found to increase with increase in temperature. The optimum temperature for the adsorption is 40oC .At higher temperature mobility of large ions of malachite green dye increases and at high temperature molecules acquire sufficient energy to undergo interaction with the active sites for adsorption. At very high temperature, it may cause swelling

effect within internal structure of char which enables large malachite green dye ions to penetrate further into it.

8. As adsorbent dose increases adsorption increases due to the availability of free sites. 100mg/100ml concentration of char is taken as the optimum adsorbate dose. As we increase adsorbate dose more than the optimum the increase in adsorption is very less and it becomes cost ineffective and there is loss of extra char.

9. The correlation coefficient,R^2 value and correspondence with experimental qe value favors pseudo 1^{st} order and thus the adsorption is assumed to be pseudo-first order with k1 = -029 and R2= .973. Moreover the qe value calculated was also near to that of experimental value.

10. The Langmuir equation assumes that there is no interaction between the adsorbate molecules and that the sorption is localized in a monolayer. It is then assumes that once a dye molecule occupies a site, no further adsorption can take place at that site. The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Both models fit well to the system with their correlation coefficients near to 1. Temkin model does not fit in.

CHAPTER-6

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